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(54) Title: A THERMOSETTING MATERIAL

(57) Abstract

The present invention relates to a thermosetting material wherein the matrix comprises at least one dendritic or hyperbranched macromolecule having a chain termination providing at least one primary or secondary reactive site. In a further aspect, the invention relates to a process for production of said material and in yet another aspect to a thermosetting resin composition providing the matrix or part of the matrix of said material. The resin composition is especially suitable for thermosetting materials such as various composites. The dendritic or hyperbranched macromolecule has a chain termination providing at least one primary or secondary reactive site and is combined with at least one conventional thermosetting resin or aliphatic, cycloaliphatic or aromatic monomeric or polymeric compound.

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A THERMOSETTING MATERIAL

The present invention relates to a thermosetting material wherein the matrix comprises at least one dendritic or hyperbranched macromolecule having a chain termination providing at least one primary or secondary reactive site and at least one other thermosetting resin or compound. In a further aspect, the invention relates to a process for production of said material and in yet another aspect to a thermosetting resin composition providing the matrix or part of the matrix of said material. The resin composition is especially suitable for thermosetting materials, being reinforced or not, such as various types of composites.

Hyperbranched and dendritic macromolecules (dendrimers) can generally be described as three dimensional highly branched molecules having a tree-like structure. Dendrimers are highly symmetric, while similar macromolecules designated as hyperbranched may to a certain degree hold an asymmetry, yet maintaining the highly branched tree-like structure. Dendrimers can be said to be monodisperse variations of hyperbranched macromolecules. Hyperbranched and dendritic macromolecules normally consist of an initiator or nucleus having one or more reactive sites and a number of branching layers of chain extending molecules and optionally a layer of one or more chain terminating molecules. The layers are usually called generations.

Composite materials can be classified in many ways depending on the identified concept. Generally can, however, a composite be classified as a material deriving its properties from two or more components which can be distinguished readily when examined in optical or electron microscopes. The strength and toughness of for instance engineering plastics are achieved by combining high strength phases such as various fibres or particles constituting a reinforcement and a ductile phase such as a resin or a resin composition constituting a matrix.

Composites are used in a wide variety of applications, each requiring specific properties from included components. The versatility of material property design and processing possibilities with thermosetting composite materials have been and will remain a major driving force for the use thereof. However, certain drawbacks still remain. Among these are some properties related to the mechanical anisotropy and often relatively high processing costs. The mechanical properties are mainly influenced by the properties, such as the toughness, of the resin matrix. Some

important applications areas of thermosetting composites and the main requirements for further mechanical improvements can be listed as in below summary.

Type of Product	Properties in Need of Improvement
Aeronautic goods and articles	Impact properties, damage tolerance
Nautic goods and articles	Moisture absorption, impact
Chemicals/chemical goods and articles	Chemical resistance, notch sensitivity
Automotive goods and articles	Low velocity impact, fatigue tolerance
Sporting goods and articles	Fatigue, impact, low velocity impact
Leisure/commodity goods and articles	Damage tolerance, low velocity impact
Electric/electronic goods and articles	Thermal shock resistance

The matrix toughness is one of the most important intrinsic properties of a thermosetting material, such as a composite, controlling various observable damages and failure mechanisms. Important mechanical properties and failure mechanisms can be summarised:

- The fatigue properties are controlled by the rate of crack growth through the material dependent of the inherent toughness and durability of the matrix and interfaces.
- The impact properties are characterised by the energy absorbed, the damage area and the residual strength after impact. Matrix toughness limits the extent of damage within the matrix thus allowing good residual strength.
- The low velocity impact property is the resistance to small impacts due to mishandling, such as dropping and stone hitting (important in automotive applications). The extent of damage is mainly controlled by the matrix toughness and adhesive properties.
- The damage tolerance and notch sensitivity are related to the presence of defects. These can originate from low velocity impacts, machining or production defaults. The further cracking of a composite material will involve a matrix cracking by traverse cracking (predominantly in 90° oriented plies) and delamination. Toughness is thus a major controlling parameter.

The matrix toughness is also important in controlling the edge effects of composite parts and the thermal loading inducing delamination. The prolongation of delamination induces matrix and possibly interfacial failures.

The plastic strain to failure can be increased by reduction of the crosslink density or the use of plasticisers. This, however, will very strongly affect the modulus and thermal properties of the material, only giving a moderate increase in toughness. The toughness can effectively be increased by addition of a second phase, such as particles. The effect of particle toughening will regardless of the particle nature, for instance stiffness and thermal transition temperature, depend on the particle size, interparticle distance and volume fraction. Suitable particles for toughening are for instance glass particles, rubber particles and thermoplastic particles having either a rigid core and a soft shell or a soft core and a rigid shell structure. These particles can have different adhesive properties to the surrounding resin matrix affecting their toughening effect and influencing the modulus of the matrix. Toughening systems also include phase separation during curing. A dispersed spherical phase is usually created in such a process. Today commonly used toughening agents are for example rubber, carboxyl terminated butadiene acrylonitrile (CTBN rubber), latex and short reactive thermoplastic chains such as polyetherimides. CTBN rubber is the most effective and most widely used toughening agent. However, it very strongly affects the thermal and mechanical properties in the resin matrix. A combination of CTBN rubber and glass particles reduces the negative effect on the mechanical properties. Polyetherimide modifiers are most recently developed systems. These systems do not affect the thermal and mechanical properties of the matrix, but are less effective as toughening agents.

Processing techniques for reinforced composites often involve a wetting stage of a reinforcing bed. The wetting is most often done using a resin in liquid state thus requiring a controlled viscosity. The viscosity should be low in order to obtain a good penetration of for instance a fibre bed, a proper wetting of the fibres and a reduced wetting time. Modified matrices generally exhibit an increased viscosity and particles are often too large to be able to freely penetrate the reinforcing bed. As a consequence, in processing techniques producing superior quality composites or allowing products having a complex geometry to be produced at high productivity rates, particles will be subject to segregation, percolation or shear field segregation. The effect of the toughening agent will therefore strongly be reduced and can even become a source of weak spots if they agglomerate to a large extent. This kind of processing include prepreging and/or impregnation techniques, such as infusion, compression transfer, vacuum moulding, transfer moulding, injection moulding, gas assisted injection moulding, structural injection moulding, filament winding, resin immersion or resin infusion. Further processing

techniques include die forming such as extrusion, rotary moulding, gravity moulding and blow moulding. Thus, the quality of the impregnation will decrease and processing times increase and even the quality of the final product may decrease. This is of course very much dependent on the particle size and to a lesser extent the particle volume fraction. The toughening effect of smaller particles is not optimal. Larger particles can be applied using an interleaf layer between plies of a composite material. This will increase the toughness of the interlamilar region where delamination occurs, but will not increase the toughness within the plies. CTBN rubber strongly increases the resin viscosity thus limiting the volume fraction that can be used.

Through the present invention it has been possible to produce a thermosetting material, such as a composite, wherein a thermosetting resin matrix having increased toughness properties without, or only slightly affecting processability, thermal and other mechanical properties, is used. The resin matrix is based on conventional thermosetting resins combined with functionalised dendritic or hyperbranched macromolecules of polyester type. As can be seen from Table 1 and the test results of Example 25, the toughening properties of these macromolecules are excellent and most important, toughening can be obtained without imparting the matrix modulus or the thermal properties.

Dendritic or hyperbranched macromolecules exhibit a spherical structure resembling that of particles. There is, however, no singularity in mechanical properties at the interface of the macromolecules and surrounding matrix as with various particles. Isolated macromolecules have in the case of phase separation, residual miscibility in the matrix, which due to the relatively high molecular weight, the unique molecular structure and large number of reactive sites will increases the toughness of the matrix. Increased matrix toughness is also seen in homogeneous matrices containing dendritic or hyperbranched macromolecules due to impacting forces being effectively distributed within the hyperbranched structure of said macromolecules. Dendritic and hyperbranched macromolecules do not or only moderately increase the viscosity and are of a small diameter despite the relatively high molecular weight. The macromolecules do not as for instance pre-shaped particles impart the processability of the system. The obtained toughening effect in a thermosetting material, such as a composite, will contrary to the interleaf technique be distributed homogeneously in all levels of the material.

The functionality and polarity of dendritic or hyperbranched macromolecules can be adapted to any resin system to provide appropriate reactive sites and phase separation properties. The macromolecules are therefore not as sensitive to different matrix chemistry as for instance polyetherimide modifiers requiring a modification of the entire matrix chemistry. The relatively high molecular weight of the dendritic or hyperbranched macromolecules, used in accordance with the present invention, makes the control of the phase separation easier.

The present invention relates to a thermosetting material, a process for production of the material and a resin composition providing the matrix or part of the matrix of said material, whereby all aspects of the invention include at least one dendritic or hyperbranched macromolecule.

The thermosetting material and thus the thermosetting resin composition, according the present invention include at least two thermosetting resins or compounds. At least one of these compounds is a chain terminated dendritic or hyperbranched macromolecule of polyester type having at least one reactive site obtained through chain termination and at least one compound is a conventional thermosetting resin or aliphatic, cycloaliphatic or aromatic compound being monomeric or polymeric. The dendritic or hyperbranched macromolecule has a chain termination providing at least one primary or secondary reactive site and the conventional resin or compound is selected from the group consisting of:

i) a monomeric or polymeric epoxide,
ii) a rubber modified monomeric or polymeric epoxide
iii) a saturated or unsaturated ester,
iv) a saturated or unsaturated polyester,
v) a hydroxyfunctional saturated or unsaturated ester,
vi) a hydroxyfunctional saturated or unsaturated polyester,
vii) a polyamine or a polyamide
viii) a bismaleimide,
ix) a phenol-formaldehyde resin,
x) a phenolic amino resin,
xi) a polyimide or polyetherimide,
xii) a melamine-formaldehyde resin,
xiii) a urea-formaldehyde resin,
xiv) an isocyanate and

xv) a urethane or a polyurethane having any of the functional groups -OH, -COOH or -NCO,

The resin composition, which in addition to said thermosetting resins or compounds optionally comprises at least one curing agent, catalyst, inhibitor or stabiliser, is cured or partially cured.

The chain terminated dendritic or hyperbranched macromolecule included in the resin composition according to the present invention is composed of a monomeric or polymeric nucleus having at least one reactive epoxide or hydroxyl group to which 1-100, preferably 1-20, generations of at least one monomeric or polymeric chain extender, whereby at least one generation includes at least one chain extender having at least two reactive hydroxyl groups and at least one reactive carboxyl group, are added. The yielded dendritic or hyperbranched macromolecule have substantially hydroxyl groups as terminal functions. The macromolecule is wholly or partly chain terminated by addition of at least one monomeric or polymeric chain stopper and/or by means of addition, oxidation, epoxidation, allylation, etherification or substitution, thereby providing the primary or secondary reactive sites.

The dendritic or hyperbranched macromolecule included in the thermosetting resin composition as well as in the thermosetting material is in different embodiments through the chain termination provided with at least one primary or secondary epoxide group, alkenyl group, amino group and/or anhydride group. The chain termination is preferably performed by means of at least one chain stopper selected from the group consisting of:

i) an unsaturated monofunctional carboxylic acid or, where applicable, an anhydride thereof,
ii) an unsaturated fatty acid,
iii) a glycidyl ester of a monofunctional carboxylic or fatty acid with 1-24 carbon atoms,
iv) a glycidyl ether of a monofunctional alcohol with 1-24 carbon atoms,
v) a carboxyfunctional unsaturated ester of a di, tri or polyfunctional carboxylic acid or, where applicable, an anhydride thereof, and
vi) an adduct between at least one mono, di, tri or polyhydroxysubstituted allyl ether and at least one mono, di, tri or polyfunctional carboxylic acid, or

is performed by means of a compound such as an epihalohydrin, preferably epichlorohydrin, or an allylhalid, preferably allylchloride and/or allylbromide. A

primary or secondary anhydride group is obtained by Michael addition of at least one unsaturated anhydride, such as maleic anhydride, to an unsaturation within the macromolecule and/or its chain termination. Michael addition is a base catalysed addition of carbanions to activated unsaturated systems.

The nucleus of said dendritic or hyperbranched macromolecule is in preferred embodiments of the present invention selected from the group consisting of

i) a mono, di, tri or polyfunctional alcohol, such as 5-ethyl-1,3-dioxane-5-methanol, 1,3-dioxane-5,5-dimethanol, neopentyl glycol, 2-ethyl-2-butyl-1,3-propanediol, cyclohexane-1,4-dimethanol, trimethylolpropane, trimethylolethane, ditrimethylolpropane, ditrimethylolethane, pentaerythritol, dipentaerythritol, tripentaerythritol, sorbitol or reaction products thereof with ethylene oxide, propylene oxide, butylene oxide and/or phenylethylene oxide (styrene oxide),

ii) a mono, di, tri or polyfunctional epoxide, such as a glycidyl ester of a monofunctional carboxylic acid with 1-24 carbon atoms or a glycidyl ether of a monofunctional alcohol with 1-24 carbon atoms,

iii) a mono, di or triglycidyl substituted isocyanurate,

iv) a glycidyl ether of a condensation product between at least one phenol and at least one aldehyde or ketone or an oligomer of such a condensation product,

v) a glycidyl ether of a mono, di, tri or polyfunctional alcohol or a glycidyl ether of a reaction product of any of said alcohols and ethylene oxide, propylene oxide, butylene oxide and/or phenylethylene oxide (styrene oxide).

The chain extender used in these preferred embodiments is a dihydroxyfunctional monocarboxylic acid, such as 2,2-dimethylolpropionic acid.

The conventional resin or compound included in the thermosetting resin composition as well as in the thermosetting material is in various embodiments an epoxide of formula

$$\begin{array}{ccccc} R_3 - O - R_2 & & & & R_2 - O - R_3 \\ & \diagdown & & \diagup & \\ & & N - R_1 - N & & \\ & \diagup & & \diagdown & \\ R_3 - O - R_2 & & & & R_2 - O - R_3 \end{array}$$

wherein

R_1 is cycloalkanyl, branched cycloalkanyl, aryl, branched aryl, linear or branched alkanylaryl; R_2 independently is linear or branched alkanyl, alkenyl or alkynyl; and

wherein R_3 independently is H or $\underset{\diagdown O \diagup}{R_4 - R_5}$

wherein
R_4 is CH or C_2-C_{10} linear or branched alkanyl, alkenyl or alkynyl and R_5 is CH_2 or C_2-C_{10} linear or branched alkanyl, alkenyl or alkynyl, whereby at least one substituent R_3 is $\underset{\diagdown O \diagup}{R_4 - R_5}$

The conventional resin or compound can alternatively be an epoxide of formula

$$R_3 - O - R_2 - R_1 - R_2 - O - R_3$$

wherein
R_1 is cycloalkanyl, branched cycloalkanyl, aryl, branched aryl, linear or branched alkanylaryl; R_2 independently is NH, linear or branched alkanyl, alkenyl or alkynyl and wherein R_3 independently is H or $\underset{\diagdown O \diagup}{R_4 - R_5}$

wherein
R_4 is CH or C_2-C_{10} linear or branched alkanyl, alkenyl or alkynyl and R_5 is CH_2 or C_2-C_{10} linear or branched alkanyl, alkenyl or alkynyl, whereby at least one substituent R_3 is $\underset{\diagdown O \diagup}{R_4 - R_5}$.

The conventional resin or compound is in preferred embodiments of the invention selected from the group consisting of

i) an epoxide, such as a glycidyl ether, of a condensation product between at least one phenol and at least one aldehyde or ketone or an oligomer of such a condensation product or
ii) an unsaturated ester or polyester having maleate, vinyl and/or allyl unsaturation.

The suitable weight ratio between dendritic or hyperbranched macromolecule provided with primary reactive, dendritic or hyperbranched macromolecule provided with secondary reactive sites and conventional resin or compound can be expressed as X:Y:Z, wherein X is 0 to 90, preferably 0.5 to 60, Y is 0 to 90, preferably 0.5 to 60, Z is 1 to 99, preferably 1 to 60, X + Y is more than or equal to 1, preferably 1 to 60, and wherein X + Y + Z equals 100. The most preferred ratio between dendritic or hyperbranched macromolecule and conventional resin or

compound is to be found within the weight ratio of 1:99 to 30:70, preferably 5:95 to 25:75.

The composite is in certain embodiments of the thermosetting material according to the present invention a decorative or an industrial laminate, which may contain at least one sheet or web of paper or glass fibre as reinforcement and/or base material.

The surface of the thermosetting material can, in specific applications of embodiments of the present invention, be metal plated or metal clad, such as copper clad laminates for printed circuits and aeronautical parts.

The thermosetting material according to the present invention is in preferred embodiments a composite containing fibres in the form of a web, a cloth, a sheet, threads or cut fibres as reinforcement material. The fibres are preferably selected among glass fibres, carbon fibres, aramide fibres and organic fibres.

The thermosetting material can in further embodiments of the present invention be a so called prepreg in the form of a roll, a sheet, a web or a cloth obtained by impregnation with the thermosetting resin composition, according to the present invention, followed by a partially curing of the resin to a so called B-stage.

The thermosetting material according to the present invention can in yet further embodiments advantageously be a moulding powder containing at least one filler; pigment or lubricant; a protective and/or decorative primer or top coat; or a thermosetting adhesive or glue.

The thermosetting material and resin composition according to the invention can advantageously be used in the production of goods and articles within aeronautical, nautical, chemical, automotive, sporting, leisure and commodity as well as for applications within the electric and electronic industry.

The process for production of the thermosetting material according to the invention is characterised in that the material is obtained by moulding a thermosetting resin composition as disclosed above, which resin composition is fully cured. This can in certain embodiments be obtained in that two or more prepregs in the form of a sheet, a web, a cloth, threads or cut fibres of glass fibre,

carbon fibre, aramide fibre, organic fibres such as cellulose impregnated with the thermosetting composition and partially cured to a so called B-stage are laminated together under heat and/or pressure.

Various embodiments of the process according to the invention include

- that glass fibres, carbon fibres, aramide fibres, organic fibres, such as cellulose, or the like are pre-shaped to a bed which is then impregnated with the resin composition by infusion, compression transfer, injection or the like, whereupon the resin is cured;
- that a bundle, tow, tape or the like of glass fibres, carbon fibres, aramide fibres, organic fibres or the like is impregnated with the resin composition whereupon said bundle, tow or tape after an optional drying is wound on a core to form a structural part, followed by curing of the resin;
- that glass fibres, carbon fibres, aramide fibres, organic fibres or the like are impregnated with the resin composition which is added to a mould, the mould being rotated to form the moulded material by means of polar gravity force;
- that the moulded material is obtained by spraying the resin composition onto or into a pre-shaped mould whereupon the resin is cured; and
- that the thermosetting product is obtained by injection moulding or compression moulding.

Disclosed and other objects and the attendant advantages will be more fully understood from enclosed embodiment Examples 1-25 and enclosed Table 1, wherein:

- Examples 1 and 2 relate to preparation of hyperbranched macromolecules.
- Examples 3-8, 22 and 24 relate to chain termination of the hyperbranched macromolecules of Examples 1 and 2. The chain termination provides the macromolecules with primary or secondary reactive sites.
- Examples 9-15 relate to preparation of thermosetting resin compositions wherein macromolecules from Examples 3-8 are included.
- Example 16 is a comparative example wherein a thermosetting resin composition outside the scope of the invention is prepared.
- Example 17 relate to preparation by moulding of thermosetting materials based on the thermosetting compositions of Examples 9-16.
- Examples 18-21 relate to evaluations of the thermosetting materials prepared by moulding according to Example 17.

- Example 23 relates to preparation of a polymeric chain stopper used in Example 24 to provide the product of Example 22 with alkenyl groups in form of allyl unsaturation.
- Example 25 relates to preparation and evaluation of an unsaturated resin composition comprising the product of Example 24.

Table 1 presents results obtained in Examples 18-21 with moulded materials based on resin compositions according to Examples 9-16.

While particular embodiments of the invention is shown in the embodiment Examples, it will be understood, of course, that the invention is not limited thereto since many modifications may be made, and it is, therefore, contemplated to cover by the appended claims any such modifications as fall within the true spirit and scope of the invention.

Example 1

A hyperbranched polyester of 2 generations was prepared from an ethoxylated pentaerythritol and 2,2-dimethylolpropionic acid.

308.9 g (0.85 mole) of pentaerythritol pentaethoxylate (Polyol PP 50, Perstorp Polyols, Sweden), 460.5 g (3.42 moles) of 2,2-dimethylolpropionic acid (Bis-MPA, Perstorp Polyols, Sweden) and 0.46 g (0.004 mole) of H_2SO_4 (96%-w/w) were charged in a 4-necked reaction flask equipped with stirrer, pressure gauge, cooler and receiver. The temperature was raised to 120°C, at which temperature 2,2-dimethylolpropionic acid began to melt and esterification water was formed. The temperature was thereafter during 20 minutes raised to 140°C, giving a transparent solution, whereby a vacuum of 30-50 mm Hg was applied. The reaction was, under stirring, allowed to continue for 4 hours, after which time the acid value was determined to be 7.0 mg KOH/g. 460.5 g (6.84 moles) of 2,2-dimethylolpropionic acid and 0.7 g (0.007 mole) of H_2SO_4 (96%-w/w) were now during 15 minutes added to the reaction mixture. A vacuum of 30-50 mm Hg was applied when charged 2,2-dimethylolpropionic acid was dissolved. The reaction was now allowed to continue for a further 4 hours giving a final acid value of ≈ 10 mg KOH/g.

Obtained product exhibited the following properties:

Acid value, mg KOH/g:	10.2
Hydroxyl value, mg KOH/g:	500
Theoretical hydroxyl value, mg KOH/g:	511
Molecular weight, g/mole:	1824
Theoretical molecular weight, g/mole:	1748

Example 2

A hyperbranched polyester of 3 generations was prepared by adding a third generation to the product of Example 1.

600.0 g of the hyperbranched polyester according to Example 1, 717.0 g (5.35 moles) of 2,2-dimethylolpropionic acid and 0.7 g (0.007 mole) of H_2SO_4 (96%-w/w) were charged in a 4-necked reaction flask equipped with stirrer, pressure gauge, cooler and receiver. The temperature was raised to 120°C, at which temperature 2,2-dimethylolpropionic acid began to melt and esterification water was formed. The temperature was thereafter during 20 minutes raised to 140°C, giving a transparent solution, whereby a vacuum of 30-50 mm Hg was applied. The reaction was now under stirring allowed to continue for 5 hours giving a final acid value of ≈ 10 mg KOH/g.

Obtained product exhibited the following properties:

Acid value, mg KOH/g:	10.6
Hydroxyl value, mg KOH/g:	493
Theoretical hydroxyl value, mg KOH/g:	498
Molecular weight, g/mole:	3311
Theoretical molecular weight, g/mole:	3608

Example 3

A chain stopped hyperbranched polyester was produced from the product of Example 2 and oleic acid.

251.2 g of the hyperbranched polyester according to Example 2, 592.3 g of oleic acid, 1.0 g of an inorganic catalyst (Fascat® 4100, Atochem, the Netherlands), 0.5 g of $Ca(OH)_2$ and 55 g of xylene were charged in a 4-necked reaction flask equipped with stirrer, nitrogen inlet, cooler and water trap (Dean-Stark).
The temperature was during 65 minutes raised to 220°C, at which temperature reaction water was formed. The reaction was now allowed to continue until an acid value of < 9 mg KOH/g was reached. The reaction time at 220°C was 420 minutes. The polyester was finally filtered using a small amount of a filter aid (Celite) to remove residual catalysts and formed calcium soaps.

Obtained product exhibited the following properties:

Theoretical molecular weight, g/mole:	11600
Final acid value, mg KOH/g:	8.2
Hydroxyl value, mg KOH/g:	8.0
Viscosity, 23°C, mPas:	3090
Non-volatile content, %:	100.0

Example 4

A chain stopped hyperbranched polyester was produced from the product of Example 2 and oleic acid.

Example 3 was repeated with the differences:
- that 455.8 g of oleic acid were charged instead of 592.3 g and
- that the reaction at 220°C was allowed to continue until an acid value of < 5 mg KOH/g was reached. The reaction time at 220°C was 300 minutes.

Obtained product exhibited the following properties:

Theoretical molecular weight, g/mole:	9900
Final acid value, mg KOH/g:	4.7
Hydroxyl value, mg KOH/g:	37.0
Viscosity, 23°C, mPas:	7520
Non-volatile content, %:	99.8

Example 5

An epoxidised (chain terminated) hyperbranched polyester was produced from the product of Example 1 and epichlorohydrin.

100.0 g of the hyperbranched polyester according to Example 1 was charged in a 4-necked reaction flask equipped with stirrer, nitrogen inlet, cooler and water-trap (Dean-Stark). The temperature was raised to 130°C at which temperature 0.6 g BF_3 etherate was added to the reaction mixture. 195.0 g (2.11 moles) of epichlorohydrin was then during 30 minutes added at a rate sufficiently low to suppress observed exothermic reaction. The reaction was allowed to continue at 130°C for 80 minutes, after which time the temperature was decreased to 100°C and 100 ml of toluene and 100 ml of 1,4-dioxane were added. 38.7 g (0.97 mole) of NaOH was now during 60 minutes added whereupon the solution became opaque and reaction water was formed. The reaction was allowed to continue for a further 120 minutes and the reaction mixture was thereafter cooled and passed through a pressurised filter to remove precipitated NaCl. Remaining solvents and epichlorohydrin were thereafter removed by means of a rotary evaporator.

Obtained product exhibited the following properties:

Theoretical molecular weight, g/mole:	2644
Epoxy equivalent weight (EEW-value), g/equivalent:	285
Theoretical EEW-value, g/equivalent:	165
Hydrolysable chlorine content, %:	0.6
Viscosity, 23°C, mPas:	21400
Non-volatile content, %:	99.7

Example 6

An epoxidised (chain terminated) hyperbranched polyester was produced from the product of Example 2 and epichlorohydrin.

Example 5 was repeated with the differences:

- that 100.0 g of the hyperbranched polyester according to Example 2 were charged instead of the hyperbranched polyester according to Example 1 and
- that the reaction time at 130°C was 120 minutes instead of 80 minutes.

Obtained product exhibited the following properties:

Theoretical molecular weight, g/mole:	5400
Epoxy equivalent weight (EEW-value), g/equivalent:	311
Theoretical EEW-value, g/equivalent:	169
Hydrolysable chlorine content, %:	0.9

Example 7

An epoxidised (chain terminated) hyperbranched polyester with secondary epoxide groups was produced from obtained product according to Example 3 and *m*-chloroperbenzoic acid.

26.36 g of *m*-chloroperbenzoic acid and 750 ml of dichloromethane were at room temperature charged in a 3-necked reaction flask equipped with stirrer, nitrogen inlet and cooler. Obtained solution was cooled to 0°C and 38.86 g of the product according to Example 3 dissolved in 250 ml of dichloromethane were now during 60 minutes instilled. Resulting reaction mixture was at 0°C stirred during 120 minutes followed by precipitation of excess *m*-chloroperbenzoic acid. The reaction mixture was now allowed to react at room temperature for a further 18 hours. Resulting product was thereafter purified by extraction using 3 x 250 ml of 0.1 M aqueous $Na_2S_2O_3$ followed by 3 x 250 ml of saturated aqueous $NaHCO_3$. The mixture was allowed to phase separate and the organic layer was removed. The final product was thereafter recovered by removal of solvent under full vacuum at 50°C using a rotary evaporator.

Obtained product exhibited the following properties:

Epoxy equivalent weight (EEW-value), g/equivalent:	440
Theoretical EEW-value, g/equivalent:	384
Viscosity, 23°C, mPas:	7000
Non-volatile content, %:	100.0

Example 8

An epoxidised (chain terminated) hyperbranched polyester with secondary epoxide groups was produced from obtained product according to Example 4 and *m*-chloroperbenzoic acid.

26.36 g of *m*-chloroperbenzoic acid and 1500 ml of dichloromethane were at room temperature charged in a 3-necked reaction flask equipped with stirrer, nitrogen inlet and cooler. Obtained solution was cooled to 0°C and 100.0 g of the product according to Example 4 dissolved in 800 ml of dichloromethane were now during 120 minutes instilled. Resulting reaction mixture was at 0° stirred during 120 minutes followed by precipitation of excess *m*-chloroperbenzoic acid. The reaction mixture was now allowed to react at room temperature for a further 16.5 hours. Resulting product was thereafter purified by extraction using 3 x 700 ml of 0.1 M aqueous $Na_2S_2O_3$ followed by 2 x 250 ml of saturated aqueous $NaHCO_3$. The mixture was allowed to phase separate and the organic layer was removed. The final product was thereafter recovered by removal of solvent under full vacuum at 50°C using a rotary evaporator.

Obtained product exhibited the following properties:

Epoxy equivalent weight (EEW-value), g/equivalent:	436
Theoretical EEW-value, g/equivalent:	429
Viscosity, 23°C, mPas:	30000
Non-volatile content, %:	100.0

Example 9

A thermosetting resin composition was prepared by mixing the product according to Example 5 with a commercial epoxide of bisphenol-F type (Araldite®, LY 5082, Ciba-Geigy, Switzerland) having a functionality of 2 and a commercial isophorone diamine curing agent (Hardener HY 5083, Ciba-Geigy, Switzerland) having a functionality of 4. The components were mixed at 23°C using mechanical stirring for 5 minutes. The resin was subsequently degassed at 23°C in a vacuum chamber at 0.1 bar for 10 minutes.

The resin composition had the following formulation and properties:

Product according to Example 5, g:	25.0
Commercial epoxide, g:	75.0
Curing agent, g:	21.3
Amine:epoxide (molar ratio):	1:1
Non-volatile content, %:	100.0
Viscosity at 25°C, mPas:	800

Example 10

Example 9 was repeated with the difference that the product according to Example 5 was replaced by the product according to Example 6.

The resin composition had the following formulation and properties:

Product according to Example 6, g:	25.0
Commercial epoxide, g:	75.0
Curing agent, g:	20.6
Amine:epoxide (molar ratio):	1:1
Non-volatile content, %:	100.0
Viscosity at 25°C, mPas:	900

Example 11

Example 9 was repeated with the difference that the product according to Example 5 was replaced by a substantially reduced percentage of the product according to Example 7.

The resin composition had the following formulation and properties:

Product according to Example 7, g:	1.0
Commercial epoxide, g:	99.0
Curing agent, g:	22.7

Amine:epoxide (molar ratio):	1:1
Non-volatile content, %:	100.0
Viscosity at 25°C, mPas:	600

Example 12

Example 9 was repeated with the difference that the product according to Example 5 was replaced by a reduced percentage of the product according to Example 7.

The resin composition had the following formulation and properties:

Product according to Example 7, g:	5.0
Commercial epoxide, g:	95.0
Curing agent, g:	22.6
Amine:epoxide (molar ratio):	1:1
Non-volatile content, %:	100.0
Viscosity at 25°C, mPas:	700

Example 13

Example 9 was repeated with the difference that the product according to Example 5 was replaced by the product according to Example 8.

The resin composition had the following formulation and properties:

Product according to Example 8, g:	5.0
Commercial epoxide, g:	95.0
Curing agent, g:	22.3
Amine:epoxide (molar ratio):	1:1
Non-volatile content, %:	100.0
Viscosity at 25°C, mPas:	600

Example 14

Example 9 was repeated with the difference that the product according to Example 5 was replaced by a reduced percentage of the product according to Example 8.

The resin composition had the following formulation and properties:

Product according to Example 8, g:	15.0
Commercial epoxide, g:	85.0
Curing agent, g:	21.0
Amine:epoxide (molar ratio):	1:1
Non-volatile content, %:	100.0
Viscosity at 25°C, mPas:	1100

Example 15

Example 9 was repeated with the difference that the product according to Example 5 was replaced by a combination of the products according to Examples 5 and 8.

The resin composition had the following formulation and properties:

Product according to Example 5, g:	25.0
Product according to Example 8, g:	5.0
Commercial epoxide, g:	70.0
Curing agent, g:	20.7
Amine:epoxide (molar ratio):	1:1
Non-volatile content, %:	100.0
Viscosity at 25°C, mPas:	900

Example 16 (Comparative Example)

A thermosetting resin composition was prepared by mixing a commercial epoxide of bisphenol-F type (Araldite® LY 5082, Ciba-Geigy, Switzerland) having a functionality of 2 with a commercial isophorone diamine curing agent (Hardener HY 5083, Ciba-Geigy, Switzerland) having a functionality of 4. The components

were mixed at 23°C using mechanical stirring for 5 minutes. The resin was subsequently degassed at 23°C in a vacuum chamber at 0.1 bar for 10 minutes.

The resin composition had the following formulation and properties:

Commercial epoxide, g:	100.0
Curing agent, g:	23.0
Amine:epoxide (molar ratio):	1:1
Non-volatile content, %:	100.0
Viscosity at 25°C, mPas:	600

Example 17

Thermosetting resin compositions according to examples 9-16 were at 23°C poured into steel moulds having the internal dimensions 110 x 27 x 2.5 mm and 27 x 25 x 10 mm, respectively. The moulds were pre-treated with a silicone based mould release agent. The resin compositions were cured in the moulds, resulting in moulded plastic specimens having dimensions equal to the internal dimensions of the moulds. Curing was performed in an oven with circulating air.

Schedule:	Heating:	23 - 80°C, gradient 3°C/minute
	Curing:	80°C during 900 minutes
	Cooling:	80- 23°C, gradient 6°C/minute

Example 18

Samples were cut out from the plastic specimens produced from resin compositions of Examples 9-11, 13 and 15-16, which resin compositions were moulded and cured in 110 x 27 x 2.5 mm moulds in accordance with Example 17. Cutting was made by a rotating saw blade and the edges of the samples were polished with a 240 grid sand paper and rinsed with demineralised water. The samples were subsequently dried and aged at 23°C in air for at least 7 days. Chips were using a razor blade prior to testing cut from the samples.

The Glasstransition Temperatures (Tg) were recorded by means of a Perkins-Elmer DSC7 (Differential Scanning Colorimeter) apparatus using the following parameters:

Average sample weight, mg:	20
Temperature range, °C:	0 - 130
Heating gradient, °C/minute:	10
Cooling gradient, °C/minute:	150
Stabilisation time at 0°C, minute:	5
Heating gradient, °C/minute:	10

Obtained results are given in Table 1.

Example 19

Samples having the dimensions 100 x 12 x 2.5 mm were cut from the plastic specimens produced from the resin compositions of Examples 9-16, which resin compositions were moulded and cured in 110 x 27 x 2.5 mm mould in accordance with Example 17. Cutting was made by a rotating saw blade and the edges of the samples were polished with a 400 grid sand paper.

The Tensile Modulus (E) were recorded by means of a Zwick Screw tensile testing apparatus equipped with an extensometer.

The following parameters were used:

Extensometer gauge length, mm:	35
Length between grips, mm:	70
Crosshead rate, mm/minute:	2

Obtained results are given in Table 1.

Example 20

Samples were, using a rotary saw blade, cut from the plastic specimens produced from the resin compositions of Examples 9-16, which resin compositions were moulded and cured in 27 x 25 x 10 mm moulds in accordance with Example 17.

The samples were cut to the exterior dimensions 25 x 25 x 10 mm and machined for Compact Tension tests according to ASTM E399.

Critical Stress Intensity Factors (K_{1c}) according to ASTM E399 were recorded on a Zwick Screw tensile testing apparatus using a crosshead rate of 0.5 mm/min. Obtained results are given in Table 1.

Example 21

The Fracture Energy (G_{1c}) were determined from the results obtained in examples 19 and 20 according to the following equation:

$$G_{1c} = \frac{K_{1c}^2}{E}\left(1 - \upsilon^2\right)$$

wherein
G_{1c} = Fracture Energy (J/m^2)
K_{1c} = Critical Stress Intensity Factor ($MPa.m^{½}$)
E = Tensile Modulus (GPa)
υ = Poisson Ratio

Obtained results are given in Table 1.

Example 22

A chain stopped hyperbranched polyester was produced from the product of Example 1 and caprylic/capric acid.

830.0 g of the of the hyperbranched polyester according to Example 1, 677.7 g (4.59 moles) of a mixture of caprylic and capric acid, 2.0 g (0.03 mole) of $Ca(OH)_2$ and 75 g of xylene were charged in a 4-necked reaction flask equipped with stirrer, nitrogen inlet, cooler and water trap (Dean-Stark). The reaction mixture was during 50 minutes heated to 170°C, whereby esterification water began to evaporate. The temperature was now during 120 minutes raised from 170°C to 210°C, giving a temperature gradient of 0.3°C/minute. The esterification was allowed to continue under stirring for 510 minutes until an acid value of < 6 mg KOH/g was obtained. Xylene was thereafter removed by a 20 minutes vacuum evaporation.

Obtained product exhibited the following properties:

Final acid value, mg KOH/g:	4.2
Hydroxyl value, mg KOH/g:	111
Viscosity, 23°C, mPas:	127
Non-volatile content, %:	99.3

Example 23

A carboxyfunctional chain stopper was prepared from trimethylolpropane diallyl ether and succinic anhydride.

502.2 g (3.20 moles) of trimethylolpropane diallyl ether (TMPDE-80, Perstorp Polyols, Sweden) and 207 g (2.07 moles) of succinic anhydride were charged in a 4-necked reaction flask equipped with a magnetic stirrer, nitrogen inlet and a cooler. The reaction mixture was during 120 minutes heated to 130°C and kept at this temperature for a further 120 minutes. Obtained product was thereafter cooled to room temperature.

Obtained product exhibited the following properties:

Acid value, mg KOH/g:	368
Hydroxyl value, mg KOH/g:	390
Viscosity, 23°C, mPas:	46

Example 24

An unsaturated polyester was prepared from the products of Example 22 and Example 23.

400.0 g of the product according to Example 22, 180.0 g of the product according to Example 23, 1.4 g of H_2SO_4 (96%-w/w) and 48 g of heptane were charged in a 4-necked reaction flask equipped with stirrer, nitrogen inlet, cooler and water trap (Dean-Stark). The reaction mixture was during 30 minutes heated to 120°C, whereby esterification water began to evaporate. The esterification was allowed to continue at 120°C for 390 minutes until an acid value of ≈ 8 mg KOH/g was obtained. The product was now neutralised with 3.0 g of $Ca(OH)_2$. Heptane was

removed by a 20 minutes vacuum evaporation and the product was finally filtered to remove excess $Ca(OH)_2$ and formed calcium compounds.

Obtained product exhibited the following properties:

Final acid value, mg KOH/g:	4.9
Viscosity, 23°C, mPas:	13800
Non-volatile content, %:	127

Example 25

An unsaturated resin composition was prepared by mixing the product according to Example 24 with a commercial unsaturated polyester (Norpol® 20-00, Jotun A/S, Norway) and adding cobalt octoate and methyl ethyl ketone (MEK) peroxide. The components were mixed at 23°C using mechanical stirring for 5 minutes.

The resin composition was compared to said commercial polyester with said addition of cobalt octoate and MEK peroxide.

Resin Compositions	Composition 1 (Exampel 24)	Composition 2 (Comparative)
Commercial polyester, g	95.0	100.0
Product according to Example 24, g:	5.0	---
Cobalt octoate (12% Co), g:	1.0	1.0
MEK peroxide, g:	1.0	1.0

The resin compositions (Compositions 1 and 2) were moulded and cured in 27 x 25 x 10 mm and 110 x 27 x 2.5 mm moulds.

Curing schedule
23°C - 20 minutes
80°C - 160 minutes

i) Samples were, using a rotary saw blade, cut from specimens cured in 27 x 25 x 10 mm moulds. The samples were cut to the exterior dimensions 25 x 25 x 10 mm and machined for Compact Tension tests according to ASTM E399. Critical Stress Intensity Factors (K_{1c}) according to ASTM E399 were

recorded on a Zwick Screw tensile testing apparatus using a crosshead rate of 0.5 mm/minutes.

ii) Samples having the dimensions 100 x 12 x 2.5 mm were cut from the specimens cured in 110 x 27 x 2.5 mm moulds. Cutting was made by a rotating saw blade and sample edges were polished with a 400 grid sand paper. The Tensile Modulus (E) were recorded by means of a Zwick Screw tensile testing apparatus equipped with an extensometer.

The following parameters were used:

Extensometer gauge length, mm:	35
Length between grips, mm:	70
Crosshead rate, mm/minute:	2

Test Result

Composition 1 (Example 24): K_{1c} = 0.98 MPa.m^{½} E = 2.9 GPa
Composition 2 (Comparative): K_{1c} = 0.62 MPa.m^{½} E = 2.5 GPa

TABLE 1

Results obtained in Examples 18 - 21.

Moulded Material Based on Resin from Example	9	10	11	12	13	14	15	Comp. Ex. 16
Tg, °C	64	67	85	85	86	85	68	84
E, GPa	3.1	2.9	3.1	2.9	3.9	2.4	2.8	3.0
K_{1c}, MPa.m^{½}	0.83	1.37	0.79	1.34	1.47	2.03	1.58	0.63
G_{1c}, J/m^2	0.20	0.57	0.18	0.55	0.63	1.52	0.79	0.11

Tg = Glasstransition Temperature
E = Tensile Modulus
K_{1c} = Critical Stress Intensity Factor
G_{1c} = Fracture Energy

Table 1 and the test result of Example 25 show that moulded materials obtained by using a thermosetting composition according to the invention (Examples 9-15 and Composition 1 of Example 25) have a very high degree of toughening compared to the unmodified thermosetting composition (Example 16 and Composition 2 of Example 25). Materials exhibiting the highest value for the Tensile Modulus (E) together with the highest value for the Critical Stress Intensity Factor (K_{1c}) is considered to be the product with the best properties. The thermosetting compositions according to Examples 13 and 14 gave for example by far the best result among evaluated epoxides and Composition 1 of Example 25 gave a test excellent result.

CLAIMS

1. A thermosetting material
c h a r a c t e r i s e d i n
that the thermosetting material is made of a cured or partially cured thermosetting resin composition, which composition comprises at least two thermosetting resins or compounds, of which at least one is a chain terminated dendritic or hyperbranched macromolecule of polyester type having at least one reactive site obtained through chain termination and of which at least one is a conventional thermosetting resin or aliphatic, cycloaliphatic or aromatic compound being monomeric or polymeric, whereby

   a) the dendritic or hyperbranched macromolecule has
      i) a chain termination providing at least one primary reactive site, or
      ii) a chain termination providing at least one secondary reactive site, and
   b) the conventional resin or compound is selected from the group consisting of
      i) a monomeric or polymeric epoxide,
      ii) a rubber modified monomeric or polymeric epoxide,
      iii) a saturated or unsaturated ester,
      iv) a saturated or unsaturated polyester,
      v) a hydroxyfunctional saturated or unsaturated ester,
      vi) a hydroxyfunctional saturated or unsaturated polyester,
      vii) a polyamine or a polyamide
      viii) a bismaleimide,
      ix) a phenol-formaldehyde resin,
      x) a phenolic amino resin,
      xi) a polyimide or polyetherimide,
      xii) a melamine-formaldehyde resin,
      xiii) a urea-formaldehyde resin,
      xiv) an isocyanate, and
      xv) a urethane or a polyurethane having any of the functional groups -OH, -COOH or -NCO,

and which resin composition optionally in addition to said thermosetting resins or compounds comprises at least one curing agent, catalyst, inhibitor or stabiliser.

2. A thermosetting material according to claim 1
c h a r a c t e r i s e d i n
that the dendritic or hyperbranched macromolecule through the chain termination is provided with at least one primary or secondary epoxide group.

3. A thermosetting material according to claim 1
c h a r a c t e r i s e d i n
that the dendritic or hyperbranched macromolecule through the chain termination is provided with at least one primary or secondary amino group.

4. A thermosetting material according to claim 1
c h a r a c t e r i s e d i n
that the dendritic or hyperbranched macromolecule through the chain termination is provided with at least one primary or secondary alkenyl group.

5. A thermosetting material according to any of the claims 1-4
c h a r a c t e r i s e d i n
that the dendritic or hyperbranched macromolecule is provided with at least one primary or secondary anhydride group obtained by Michael addition of at least one unsaturated anhydride to an unsaturation within the macromolecule and/or its chain termination.

6. A thermosetting material according to claim 5
c h a r a c t e r i s e d i n
that the anhydride added to the macromolecule and/or its chain termination is maleic anhydride.

7. A thermosetting material according to any of the claims 1-6
c h a r a c t e r i s e d i n
that the thermosetting material is a moulding powder comprising at least one filler, pigment or lubricant.

8. A thermosetting material according to any of the claims 1-6
c h a r a c t e r i s e d i n
that the thermosetting material is a so called prepreg obtained by a partial curing to a so called B-stage of a roll, a sheet, a web, a cloth, threads or cuttings impregnated with the thermosetting resin composition.

9. A thermosetting material according to any of the claims 1-6
characterised in
the thermosetting material is a decorative or industrial laminate.

10. A thermosetting material according to claim 9
characterised in
that the laminate is obtained by curing at least one prepreg.

11. A thermosetting material according to any of the claims 1-10
characterised in
that the thermosetting material contains fibres as reinforcement material.

12. A thermosetting material according to claim 11
characterised in
that the fibres are present in the form of a web, a cloth, a sheet, threads or cut fibres.

13. A thermosetting material according to claim 11 or 12
characterised in
that the fibres are selected from the group consisting of glass fibres, carbon fibres, aramide fibres and organic fibres, such as cellulose.

14. A thermosetting material according to any of the claims 1-6
characterised in
that the thermosetting material is a protective and/or decorative coating, such as a primer or a top coat.

15. A thermosetting material according to any of the claims 1-6
characterised in
the thermosetting material is an adhesive or a glue.

16. A thermosetting material according to any of the claims 1-15
characterised in
that the thermosetting material is used in the production of semi-finished or finished goods and articles selected from the group consisting of

i) aeronautic goods and articles,
ii) nautic goods and articles,
iii) chemicals and chemical goods and articles,
iv) automotive coatings, goods and articles,

v) sporting goods and articles,
vi) leisure and commodity goods and articles, and
vii) electric and electronic goods and articles.

17. A thermosetting material according to claim 16
c h a r a c t e r i s e d i n
that the semi-finished or finished goods or articles are produced using a processing technique selected from the group consisting of

i) resin immersion or infusion,
ii) compression transfer,
iii) vacuum moulding,
iv) transfer moulding,
v) injection moulding,
vi) gas assisted injection moulding,
vii) structural injection moulding,
viii) filament winding,
ix) extrusion,
x) rotary moulding,
xi) gravity moulding, and
xii) blow moulding.

18. A thermosetting material according to claim 16 or 17
c h a r a c t e r i s e d i n
that the semi-finished or finished goods or articles have at least one metal plated or metal clad surface.

19. A process for production of a thermosetting material
c h a r a c t e r i s e d i n
that the thermosetting material is obtained by moulding and curing or partially curing a thermosetting resin composition, which resin composition comprises at least two thermosetting resins or compounds, of which at least one is a chain terminated dendritic or hyperbranched macromolecule of polyester type having at least one reactive site obtained through chain termination and of which at least one is a conventional thermosetting resin or aliphatic, cycloaliphatic or aromatic compound being monomeric or polymeric, whereby

a) the dendritic or hyperbranched macromolecule has

i) a chain termination providing at least one primary reactive site, or
ii) a chain termination providing at least one secondary site, and

b) the conventional resin or compound is selected from the group consisting of

i) a monomeric or polymeric epoxide,
ii) a rubber modified monomeric or polymeric epoxide,
iii) a saturated or unsaturated ester,
iv) a saturated or unsaturated polyester,
v) a hydroxyfunctional saturated or unsaturated ester,
vi) a hydroxyfunctional saturated or unsaturated polyester,
vii) a polyamine or a polyamide
viii) a bismaleimide,
ix) a phenol-formaldehyde resin,
x) a phenolic amino resin,
xi) a polyimide or polyetherimide,
xii) a melamine-formaldehyde resin,
xiii) a urea-formaldehyde resin,
xiv) an isocyanate, and
xv) a urethane or a polyurethane having any of the functional groups -OH, -COOH or -NCO,

and which resin composition optionally in addition to said thermosetting resins or compounds comprises at least one curing agent, catalyst, inhibitor or stabiliser.

20. A process according to claim 19
characterised in
that two or more prepregs are laminated together under heat and/or pressure, which prepregs are made from a sheet, a web, a cloth, threads or cuttings of glass fibres, carbon fibres, aramide fibres or organic fibres such as cellulose, impregnated with the thermosetting resin composition and partially cured to a so called B-stage.

21. A process according to claim 19
characterised in
that glass fibres, carbon fibres, aramide fibres or organic fibres such as cellulose, are pre-shaped to a bed which is then impregnated with the resin composition by infusion, compression transfer, vacuum moulding, transfer

moulding, injection moulding, gas assisted injection moulding or structural injection moulding, after which the resin composition is cured.

22. A process according to claim 19
characterised in
that a bundle, tow, tape or the like made of glass fibres, carbon fibres, aramide fibres or organic fibres such as cellulose, is impregnated with the resin composition whereupon said bundle, tow or tape after an optional drying is wound on a core to form a structural part, after which the resin composition is cured.

23. A process according to claim 19
characterised in
that glass fibres, carbon fibres, aramide fibres or organic fibres such as cellulose are impregnated with the resin composition which is added to a mould, the mould being rotated to form a moulded material by means of polar gravity force, after which the resin composition is cured.

24. A process according to claim 19
characterised in
that a moulded thermosetting material is obtained by spraying the resin composition onto or into a pre-shaped mould, after which the resin composition is cured.

25. A process according to claim 19
characterised in
that a thermosetting material is obtained by a continuous die forming procedure, such as injection moulding, compression moulding, rotary moulding, gravity moulding, blow moulding or extrusion, optionally including curing of the resin composition.

26. A thermosetting resin composition
characterised in
that it includes at least two thermosetting resins or compounds, of which at least one is a chain terminated dendritic or hyperbranched macromolecule of polyester type having at least one reactive site obtained through chain termination and of which at least one is a conventional thermosetting resin or aliphatic, cycloaliphatic or aromatic monomeric or polymeric compound whereby

a) the dendritic or hyperbranched macromolecule has
   i) a chain termination providing at least one primary reactive site, or
   ii) a chain termination providing at least one secondary reactive site, and
b) the conventional resin or compound is selected from the group consisting of
   i) a monomeric or polymeric epoxide,
   ii) a rubber modified monomeric or polymeric epoxide,
   iii) a saturated or unsaturated ester,
   iv) a saturated or unsaturated polyester,
   v) a hydroxyfunctional saturated or unsaturated ester,
   vi) a hydroxyfunctional saturated or unsaturated polyester,
   vii) a polyamine or polyamide
   viii) a bismaleimide,
   ix) a phenol-formaldehyde resin,
   x) a phenolic amino resin,
   xi) a polyimide or polyetherimide,
   xii) a melamine-formaldehyde resin,
   xiii) a urea-formaldehyde resin,
   xiv) an isocyanate and
   xv) a urethane or a polyurethane having any of the functional groups -OH, -COOH or -NCO,

which resin composition in addition to said thermosetting resins or compounds optionally comprises at least one curing agent, catalyst, inhibitor or stabiliser.

27. A resin composition according to claim 26
c h a r a c t e r i s e d i n
that the chain terminated dendritic or hyperbranched macromolecule is composed of a monomeric or polymeric nucleus having at least one reactive epoxide or hydroxyl group to which 1-100, preferably 1-20, generations of at least one monomeric or polymeric chain extender, whereby at least one generation includes a chain extender having at least two reactive hydroxyl groups and at least one reactive carboxyl group, are added, that terminal functions of said macromolecule substantially are hydroxyl groups and that the macromolecule wholly or partly is chain terminated by at least one monomeric or polymeric chain stopper and/or by means of addition,

oxidation, epoxidation or allylation, thereby providing the primary or secondary reactive sites.

28. A resin composition according to claim 26 or 27
c h a r a c t e r i s e d i n
that the chain termination provides the dendritic or hyperbranched macromolecule with at least one primary or secondary epoxide group.

29. A resin composition according to claim 26 or 27
c h a r a c t e r i s e d i n
that the chain termination provides the dendritic or hyperbranched macromolecule with at least one primary or secondary amino group.

30. A resin composition according to claim 26 or 27
c h a r a c t e r i s e d i n
that the chain termination provides the dendritic or hyperbranched macromolecule with at least one primary or secondary alkenyl group.

31. A resin composition according to any of the claims 26-30
c h a r a c t e r i s e d i n
that the dendritic or hyperbranched macromolecule is provided with at least one primary or secondary anhydride group obtained by Michael addition of at least one unsaturated anhydride to an unsaturation within the macromolecule and/or its chain termination.

32. A thermosetting material according to claim 31
c h a r a c t e r i s e d i n
that the anhydride added to the macromolecule and/or its chain termination is maleic anhydride.

33. A resin composition according to claim 26 or 27
c h a r a c t e r i s e d i n
that the chain termination is performed by means of at least one chain stopper selected from the group consisting of

i) an unsaturated monofunctional carboxylic acid or, where applicable, an anhydride thereof,
ii) an unsaturated fatty acid,
iii) a glycidyl ester of a monofunctional carboxylic or fatty acid having 1-24 carbon atoms,

iv) a glycidyl ether of a monofunctional alcohol having 1-24 carbon atoms,
v) a carboxyfunctional unsaturated ester of a di, tri or a polyfunctional carboxylic acid or, where applicable, an anhydride thereof, and
vi) an adduct between at least one mono, di, tri or polyhydroxysubstituted allyl ether and at least one mono, di, tri or polycarboxylic acid.

34. A resin composition according to claim 26 or 27
characterised in
that the chain termination is performed by means of epoxidation using an epihalohydrin.

35. A resin composition according to claim 34
characterised in
that the epihalohydrin is epichlorohydrin.

36. A resin composition according to claim 26 or 27
characterised in
that the chain termination is performed by means of allylation using an allylhalid.

37. A resin composition according to claim 36
characterised in
that the allylhalid is allylchloride and/or allylbromide.

38. A resin composition according to claim 27
characterised in
that the nucleus is a mono, di, tri or polyfunctional alcohol.

39. A resin composition according to claim 38
characterised in
that the di, tri or polyfunctional alcohol is selected from the group consisting of

i) 5-ethyl-1,3-dioxane-5-methanol,
ii) 1,3-dioxane-5,5-dimethanol,
iii) neopentyl glycol,
iv) 2-ethyl-2-butyl-1,3-propanediol,
v) cyclohexane-1,4-dimethanol,
vi) trimethylolpropane,
vii) trimethylolethane,

viii) ditrimethylolpropane,
ix) ditrimethylolethane,
x) pentaerythritol,
xi) dipentaerythritol,
xii) tripentaerythritol, and
xiii) sorbitol.

40. A resin composition according to claim 27
characterised in
that the nucleus is a reaction product between a mono, di, tri or polyfunctional alcohol and ethylene oxide, propylene oxide, butylene oxide or phenylethylene oxide.

41. A resin composition according to claim 27
characterised in
that the nucleus is a mono, di, tri or polyfunctional epoxide.

42. A resin composition according to claim 41
characterised in
that the epoxide is a glycidyl ester of a monofunctional carboxylic acid having 1-24 carbon atoms

43. A resin composition according to claim 41
characterised in
the epoxide is a glycidyl ether of a monofunctional alcohol having 1-24 carbon atoms.

44. A resin composition according to claim 41
characterised in
that the epoxide is a glycidyl ether of a di, tri or polyfunctional alcohol.

45. A resin composition according to claim 41
characterised in
that the epoxide is a mono, di or triglycidyl substituted isocyanurate.

46. A resin composition according to claim 41
characterised in
that the epoxide is a glycidyl ether of a condensation product between at least one phenol and at least one aldehyde or an oligomer of such a condensation product.

47. A resin composition according to claim 41
c h a r a c t e r i s e d i n
that the epoxide is a glycidyl ether of a condensation product between at least one phenol and at least one ketone or an oligomer of such a condensation product.

48. A resin composition according to claim 41
c h a r a c t e r i s e d i n
that the epoxide is a glycidyl ether of a reaction product between at least one mono, di, tri or polyfunctional alcohol and ethylene, propylene, butylene and/or phenylethylene oxide.

49. A resin composition according to claim 27
c h a r a c t e r i s e d i n
that the chain extender is a dihydroxyfunctional monocarboxylic acid.

50. A resin composition according to claim 49
c h a r a c t e r i s e d i n
that the chain extender is 2,2-dimethylolpropionic acid.

51. A resin composition according to claim 26
c h a r a c t e r i s e d i n
that the conventional resin or compound is an epoxide of formula:

$$\begin{array}{ccccc} R_3 - O - R_2 & \diagdown & & \diagup & R_2 - O - R_3 \\ & & N - R_1 - N & & \\ R_3 - O - R_2 & \diagup & & \diagdown & R_2 - O - R_3 \end{array}$$

wherein
R_1 is cycloalkanyl, branched cycloalkanyl, aryl, branched aryl, linear or branched alkanylaryl,

R_2 independently is linear or branched alkanyl, alkenyl or alkynyl, and
R_3 independently is H or $R_4 \underset{\diagdown O \diagup}{-} R_5$, wherein

R_4 is CH or C_2-C_{10} linear or branched alkanyl, alkenyl or alkynyl, and
R_5 is CH_2 or C_2-C_{10} linear or branched alkanyl, alkenyl or alkynyl,
whereby at least one substituent R_3 is $R_4 \underset{\diagdown O \diagup}{-} R_5$.

52. A resin composition according to claim 26
c h a r a c t e r i s e d i n
that the conventional resin or compound is an epoxide of formula:

$$R_3 - O - R_2 - R_1 - R_2 - O - R_3$$

wherein

R_1 is cycloalkanyl, branched cycloalkanyl, aryl, branched aryl, linear or branched alkanylaryl,
R_2 independently is NH, linear or branched alkanyl, alkenyl or alkynyl, and
R_3 independently is H or $R_4 \underset{O}{\diagdown\!-\!\diagup} R_5$, wherein

R_4 is CH or C_2-C_{10} linear or branched alkanyl, alkenyl or alkynyl, and
R_5 is CH_2 or C_2-C_{10} linear or branched alkanyl, alkenyl or alkynyl,
whereby at least one substituent R_3 is $R_4 \underset{O}{\diagdown\!-\!\diagup} R_5$.

53. A resin composition according to claim 26
c h a r a c t e r i s e d i n
that the conventional resin or compound is an epoxide.

54. A resin composition according to claim 53
c h a r a c t e r i s e d i n,
that the epoxide is a glycidyl ether of a condensation product between at least one phenol and at least one aldehyde or an oligomer of such a condensation product.

55. A resin composition according to claim 53
c h a r a c t e r i s e d i n
that the epoxide is a glycidyl ether of a condensation product between at least one phenol and at least one ketone or an oligomer of such a condensation product.

56. A resin composition according to claim 26
c h a r a c t e r i s e d i n
that the conventional resin or compound is an unsaturated ester or polyester having maleate, vinyl and/or allyl unsaturation.

57. A resin composition according to claim 26
c h a r a c t e r i s e d i n
a weight ratio of X:Y:Z between dendritic or hyperbranched macromolecule having primary reactive sites, dendritic or hyperbranched macromolecule having secondary reactive sites and conventional resin or compound, whereby X is 0 - 90, Y is 0 - 90, Z is 1 - 99, X + Y is more than or equal to 1 and whereby X + Y + Z equals 100.

58. A resin composition according to claim 57
c h a r a c t e r i s e d i n
that X + Y is 1 - 60.

59. A resin composition according to claim 57 or 58
c h a r a c t e r i s e d i n
that X is 0.5 - 60.

60. A resin composition according to claim 57 or 58
c h a r a c t e r i s e d i n
that Y is 0.5 - 60.

61. A resin composition according to claim 57
c h a r a c t e r i s e d i n
that Z is 1 - 60.

62. A resin composition according to any of the claims 26-61
c h a r a c t e r i s e d i n
a weight ratio between dendritic or hyperbranched macromolecule and conventional resin or compound of 1:99 to 30:70, preferably 5:95 to 25:75.

INTERNATIONAL SEARCH REPORT

International application No.
PCT/SE 95/01491

A. CLASSIFICATION OF SUBJECT MATTER

IPC6: C08L 67/06, C08J 5/04, C08J 5/24
According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC6: C08L, C08G

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

SE,DK,FI,NO classes as above

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

CAPLUS, WPI, EPODOC

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	WO 9318079 A1 (DSM N.V.), 16 Sept 1993 (16.09.93) --	1-62
A	WO 9317060 A1 (PERSTORP AB), 2 Sept 1993 (02.09.93) -- --------	1-62

☐ Further documents are listed in the continuation of Box C. ☒ See patent family annex.

* Special categories of cited documents:
"A" document defining the general state of the art which is not considered to be of particular relevance
"E" erlier document but published on or after the international filing date
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"P" document published prior to the international filing date but later than the priority date claimed
"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
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"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
3 April 1996	10 -04- 1996

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INTERNATIONAL SEARCH REPORT

Information on patent family members

05/02/96

International application No.
PCT/SE 95/01491

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